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Staibe liquid diperoxyacid bleach.

Stable liquid bleach compositions containing diperoxyacid particles, C11-C13 linear alkylbenzene sulfonate surfactant, optional cumene sulfonate, magnesium sulfate, optional sodium or potassium sulfate, and water combined at certain carefully balanced levels and ratios. The compositions have a pH of from about 2 to about 4.5 and a viscosity of from about 50 to about 1000 cps at 20°C.

STABLE LIQUID DIPEROXYACID BLEACH

Technical Field

The present invention relates to stable liquid diperoxyacid bleach compositions useful for bleaching fabrics, hard surfaces and other substrates. The compositions contain water-insoluble aliphatic diperoxyacid particles, C₁₁- C₁₃ linear alkylbenzene sulfonate surfactant, cumene sulfonate as an optional ingredient, magnesium sulfate, sodium or potassium sulfate as an optional ingredient, and water. The compositions also have a pH of from about 2 to about 4.5 and a viscosity of from about 50 to about 1000 cps at 20°C. The ingredients are combined at certain carefully balanced levels and ratios, as hereinafter described, to provide compositions exhibiting good physical and chemical stability.

Background Art

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European Patent Application 160,342, Humphreys et al, published November 6, 1985, discloses aqueous liquid bleaching compositions containing organic peroxyacid particles suspended in an acidic surfactant-15

U.S. Patent 3,996,152, Edwards et al. issued December 7, 1976, discloses stable, low-pH gels containing peroxyacid bleach particles and a non-starch thickening agent.

U.S. Patent 4,100,095, Hutchins, issued July 11, 1978, discloses the stabilization of peroxyacid bleaches by the use of certain exotherm control agents.

Despite the above attempts to stabilize liquid diperoxyacid bleaching compositions, there is a continuing need for the development of physically and chemically stable liquid diperoxyacid bleaches having a high level

25 Summary of the Invention

The present invention relates to a stable liquid bleach composition comprising, by weight:

(a) from about 10% to about 25% of water-insoluble diperoxyacid particles of the formula HOOOC(CH₂)_nCOOOH, wherein n is from about 7 to about 14, said particles having an average size of from

(b) from about 2% to about 6%, on an acid basis, of a C11-C13 linear alkylbenzene sulfonate surfactant;

(c) from about 0% to about 8%, on an acid basis, of cumene sulfonate;

(d) from about 5% to about 15% of magnesium sulfate;

(e) from 0% to about 7% sodium or potassium sulfate; and

(f) from about 40% to about 78% water

said composition containing from about 3% to about 14% of (b) and (c), from about 5% to about 16% of (d) 35 and (e), and from about 12% to about 30% of (b), (c), (d) and (e); the weight ratio of (a) to (d) being less than about 3:1; and said composition having a pH of from about 2 to about 4.5 and a viscosity of from about 50 to

Detailed Description of the Invention

The liquid bleach compositions herein contain water-insoluble aliphatic diperoxyacid particles, C11-C13 linear alkylbenzene sulfonate surfactant, cumene sulfonate as an optional ingredient, magnesium sulfate, sodium or potassium sulfate as an optional ingredient and water. These essential ingredients are combined at certain carefully balanced levels and ratios to obtain compositions having a high level of peroxyacid bleach, low product viscosity, and good physical and chemical stability. The compositions generally remain as stable suspensions having little or no separation of ingredients during storage, preferably for as long as 2 months at room temperature. The compositions also have chemical (i.e., peroxyacid) stability of at least about 80%, with the preferred compositions having at least about 90% stability after 2 months storage at room temperature.

The compositions of the present invention have a pH of from about 2 to about 4.5, preferably from about 2.5 to about 4, most preferably from about 3 to about 3.5, when measured at 20°C for best peroxyacid bleach *50*

The compositions also have a viscosity of from about 50 to about 1000 cps, preferably from about 60 to about 750 cps, more preferably from about 75 to about 500 cps, and most preferably from about 100 to about 350 cps, at 20°C, when measured with an LTV Brookfield Viscometer, using a No. 3 spindle and a setting of 60 rpm. This relatively low viscosity is desired for convenient pouring from a container by the user.

The compositions of the present invention contain from about 10% to about 25%, preferably from about 12% to about 22%, more preferably from about 14% to about 20%, most preferably from about 15% to about 20%, by weight, of substantially water-insoluble diperoxyacid particles of the formula HOOOC(CH₂)_nCOOOH, wherein n is from about 7 to about 14, preferably from about 8 to 12. The particles have an average size of from about 0.5 to about 15, preferably from about 0.5 to about 10, microns. A particularly preferred material is 1,12-diperoxydodecanedioic acid (DPDA).

The compositions contain from about 2% to about 6%, preferably from about 2% to about 4%, by weight on an acid basis, of a water-soluble (e.g., alkali metal, ammonium or alkylolammonium) C₁₁-C₁₃ linear alkylbenzene sulfonate surfactant. The alkylbenzene sulfonate contributes to physical stability by dispersing the peroxyacid particles. However, since it also increases product viscosity, particularly when used at higher levels within the claimed range and when shorter carbon chain (e.g., C₁₁ or C₁₂) alkylbenzene sulfonates are selected, the type and level of alkylbenzene sulfonate must be selected along with the other ingredients herein to provide the desired viscosity. The C₁₃ alkylbenzene sulfonates are particularly preferred.

The compositions can also contain from 0% to about 8%, preferably from about 1% to about 6%, most preferably from about 2% to about 5%, by weight on an acid basis, of a water-soluble (e.g., alkali metal, ammonium or alkylolammonium) cumene sulfonate. Cumene sulfonate also functions as a dispersant for the peroxyacid particles, and it significantly decreases viscosity. It thus can serve as a thinning agent and as a partial replacement for the C₁₁-C₁₃ linear alkylbenzene sulfonate surfactant. In certain compositions, the cumene sulfonate represents from 0% to about 4%, preferably from about 1% to about 3%, by weight on an acid basis, of the composition.

The bleach compositions herein further contain from about 5% to about 15%, preferably from about 8% to about 12%, by weight, of magnesium sulfate. The magnesium sulfate helps to suspend the diperoxyacid particles via density matching in range of from about 1.15 to about 1.22 g/ml. Magnesium sulfate also functions as an effective exotherm control agent in the present compositions.

The compositions further contain from 0% to about 7%, preferably from about 2% to about 6%, by weight, of sodium sulfate or potassium sulfate. Sodium and potassium sulfate, and to a lesser extent the cumene sulfonate, can be used to help match the density of, and thereby suspend, the peroxyacid particles. Mixtures of sodium or potassium sulfate, cumene sulfonate and magnesium sulfate are preferred to avoid adding excessive magnesium hardness to the wash water. The mixture of these salts also appears to be more effective at physically stabilizing the peroxyacid particles since less of the mixture is required to stabilize the composition than when magnesium sulfate alone is used. However, sodium and potassium sulfate significantly increase viscosity, and so their use must be limited to meet the desired viscosity range.

Finally, the compositions contain from about 40% to about 78%, preferably from about 50% to about 70%, by weight, of water.

In addition to the above, the C₁₁-C₁₃ alkylbenzene sulfonate and cumene sulfonate together should represent from about 3% to about 14%, preferably from about 4% to about 12%, most preferably from about 4% to about 10%, by weight, of the composition to provide sufficient dispersant for the peroxyacid particles while maintaining the desired low viscosity. In certain compositions, the C₁₁-C₁₃ alkylbenzene sulfonate and cumene sulfonate together represent from about 3% to about 10%, preferably from about 3% to about 8%, most preferably from about 3.5% to about 6%, by weight of the composition.

The magnesium sulfate and sodium or potassium sulfate should represent from about 5% to about 16%, preferably from about 8% to about 16%, more preferably from about 10% to about 15%, by weight of the composition in order to adequately suspend the peroxyacid particles. The weight ratio of magnesium sulfate to sodium or potassium sulfate is preferably from about 1:1 to about 4:1, more preferably from about 2:1 to about 3:1, for the desired combination of exotherm stability, low wash water hardness, and low viscosity.

The C₁₁-C₁₃ alkylbenzene sulfonate, cumene sulfonate, magnesium sulfate and sodium or potassium sulfate together should represent from about 12% to about 30%, preferably from about 12% to about 25%, more preferably from about 14% to about 25%, most preferably from about 14% to about 20%, by weight of the composition to provide sufficient dispersing and suspending agents.

The weight ratio of diperoxyacid particles to magnesium sulfate should also be less than about 3:1, preferably less than about 2.5:1, for best exotherm stability.

The bleaching compositions of the present invention can, of course, be employed by themselves as bleaching agents. However, such compositions will more commonly be used as one element of a total bleaching or laundering composition.

Bleaching compositions herein can contain any of the optional ingredients known for use in such compositions.

The compositions herein can contain minor amounts, generally less than about 5%, preferably less than about 2%, most preferably less than about 1%, by weight, of other synthetic surfactants, such as other anionic, nonionic, cationic and zwitterionic surfactants, or mixtures thereof, known in the art. However, such additional surfactants, particularly nonionic and cationic surfactants, have been found to increase viscosity and to cause phase separation when used at higher levels, and thus are not preferred for use herein. Preferably, the compositions are substantially free of such other surfactants. The compositions herein generally contain less than about 2%, preferably less than about 1%, by weight, of other anionic synthetic surfactants. Preferably, the compositions are essentially free of such other anionic synthetic surfactants.

Since the peroxyacid compounds used in the compositions of the present invention are subject to the loss of available oxygen when contacted by heavy metals, it is desirable to include a chelating agent in the compositions. Such agents are preferably present in an amount ranging from 0.005% to about 1.0% by weight of the composition. The chelating agent can be any of the well-known agents, including those described in U.S. Patent 3,442,937, issued May 6, 1969 to Sennewald et al., U. S. Patent 2,838,459, issued July 10, 1958 to Sprout, Jr., and U.S. Patent 3,192,255, issued June 29, 1965 to Cann. Preferred chelating agents are picolinic acid and dipicolinic acid.

Bleaching compositions of the present invention are utilized by adding them to water in an amount sufficient to provide from about 1.0 ppm to 100 ppm, preferably from about 1.0 ppm to 50 ppm, available oxygen in

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solution. Generally, this amounts to about 0.01% to 0.4%, preferably from about 0.01% to 0.2%, by weight of $^{\circ}$ composition in solution. Fabrics to be bleached are then contacted with such aqueous bleaching solutions.

The compositions of the present invention can also be used in combination with conventional fabric laundering detergent compositions. Such compositions can contain standard detergent ingredients, such as the surfactants and builders described in U.S. Patent 4,100,095, Hutchins et al., issued July 11, 1978, incorporated herein by reference. Preferred detergent compositions are described in U.S. Patent 4,561,998, Wertz, et al., issued December 31, 1985, and U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both incorporated herein by reference.

Preferably, detergent compositions formulated for use with bleaching compositions herein have a pH of from about 9 to about 12, preferably from about 9.5 to about 11.5, more preferably from about 10 to about 11. They preferably contain from about 2% to about 15%, more preferably from about 4% to about 10%, by weight, of monoethanolamine. The combination of such an alkaline composition with a bleaching composition herein preferably delivers a wash water pH of from about 7.8 to about 9, preferably from about 7.9 to about 8.5, which is desired for good bleaching performance, a minimum of fabric yellowing, and a minimum of bleach decomposition by the monoethanolamine.

The following examples illustrate the compositions of the present invention.

All parts, percentages and ratios used herein are by weight unless otherwise specified.

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The following composition was prepared by high shear mixing of the components in an Eppenbach mixer while in an ice bath. The DPDA and water were added to the mixer before turning the mixer on. The suds suppressor was added to minimize foaming while mixing and to minimize air entrapment in the finish composition. The other components were added in the order listed at the indicated times after turning on the

2	Component	Grams	Wt.8	Time
	1,12-Diperoxydodecanedioic	10,821.6	18.0	
<i>30</i>	acid (DPDA) (26.68%			
e de la composition della comp	active slurry*)			
	Water (additional)	1896	11.8	0
<i>35</i>	Suds suppressor	12.8		1 min.
40	C ₁₃ linear alkylbenzene sulfonic acid (96% active	417.8	2.5	3 min.
	Sodium cumene sulfonate (50% active*)		1.45	3 min.
45	Dipicolinic acid	1.6	0.01	3 min.
2 -	Sodium sulfate		4.0	
	Magnesium sulfate			2 hr.10 min.
<i>50</i>	Sodium hydroxide (50% active*)	104		3 hr.10 min.
	*Balance primarily water.			
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After 3 hr. 30 min., the pH of the composition was determined to be 3.20 at 20°C. After 4 hr. 10 min., the pH was again determined to be 3.20 at 20°C and the mixer was turned off. The composition was a stable suspension of the ingredients. It has a viscosity of about 350 cps at about 20°C. The DPDA had an average particle size of about 2-5 microns.

The above describes the preferred process for making the composition since high shear mixing of the components in an ice bath, their order of addition and the approximate times of addition have all been found to be important to obtain the desired physical stability.

After 9 days, there still was no physical separation of the composition. A 951 gram sample of the composition was removed from the bottom and analyzed. It contained 18.29% DPDA and 10.81% magnesium

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sulfate. Since the target composition was 18.0% DPDA, chemical stability was very good.

After 11 days, about 48 grams of water were removed from the bottom of the composition. Since this

represents only about 0.3% of the composition, physical stability was very good.

After 18 days, the original composition was transferred, along with 5 other samples of similar composition and preparation, to a 55 gallon drum and mixed by hand. The mixture was analyzed to contain 18.29% DPDA. It had a viscosity of about 350 cps, a density of 1.187 g/ml, and a pH of 3.20, all measured at 20°C. The next day, samples of the mixture were placed in storage at 40°F (4.44°C), 50°F (10°C), 70°F (21.1°C), 90°F (32.2°C) and 100°F (37.8°C).

After 17 days, the samples had very good physical and chemical stability, as indicated below.

Physical Stability

40°F - OK. Very slight clear aqueous layer on top.

50°F - OK. No separation.

70°F - OK. No separation.

90°F - OK. Less than about 2% clear aqueous layer on bottom.

100°F - Less than about 5% clear aqueous layer on bottom.

Chemical Stability

50°F - 18.25% DPDA

70°F - 18.21% DPDA

90°F - 18.28% DPDA

The above composition is preferably used in combination with the following detergent composition. The detergent composition was prepared by adding the following components to a mixing tank in the order listed with continuous mixing.

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	ક	Wt. 8	Wt. 8
Components	Assay	Product	Stock
Sodium C ₁₄₋₁₅ alky poly-			
ethoxylate (2.25) sulfa	te 48.8	11.3	23.2
C ₁₃ linear alkylbenzene			-5,2
sulfonic acid	96.0	8.0	8.33
Sodium diethylenetriamine			0.33
pentaacetate	41.0	0.35	0.7
Propylene glycol	100.0	10.5	•
Monoethanolamine	100.0		10.5
Brightener mix		5.0	3.0
C ₁₂₋₁₃ alcohol polyethoxy-	100.0	=	6.21 ²
late (6.5) *			
Ethanol	100.0	9.0	7.0
	92.0	10.48	7.3
Potassium hydroxide	45.0	2.48	5.51
Sodium hydroxide	50.0	2.94	5.88
Boric Acid	100.0	1.25	1.25
Water	-	-	5.65
Sodium 2-dodecenyl			
succinate	80.0	5.53	6.9
C ₁₂₋₁₄ fatty acid	100.0	3.5	3.5
Citric acid	50.0	4.0	8.0
Calcium formate	10.0	0.12	
TEPA-E15-18**	80.0	3.0	1.2
pH trim to 10.5		3.U	3.75
Protease enzyme (2.0 AU/g)	-	-	-
	100.0	1.16	1.16

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	*	Wt. 8	Wt. %	
Components	Assay	Product	Stock	
Amylase enzyme				5
(375 AM. U/g)	100.0	0.16	0.16	
Perfume	100.0	0.25	0.25	
Dye	100.0	. 0.08	0.08	10
Water		to 100%	3.25	

¹Paste also contains 16.2% ethanol and 35% water.

²Contains 32.2% monoethanolamine, 32.2% water, 32.2%

C₁₂₋₁₃ alcohol polyethoxylate (6.5), and 3.36% of brightener.

- * Alcohol and monoethoxylated alcohol removed.
- ** Tetraethylene pentaimine ethoylated with 15-18 moles (avg.) of ethylene oxide at each hydrogen site.

The compositions are preferably used in a volume ratio of detergent composition to liquid bleach of about 5.5:1. The detergent composition is designed for a usage level of about 0.55 cups in a typical U.S. laundering process. This delivers a concentration of product in the wash water of about 0.22% by weight. Usage of about 0.1 cups (i.e., about 35 ml) of the liquid bleach would deliver about 10 ppm of available oxygen to the wash water. The detergent composition and liquid bleach are preferably simultaneously codispensed from a dual compartment bottle at a volume ratio of detergent to bleach of about 5.5:1.

The mixture of the succinate and fatty acid builders in the above detergent composition is preferred because it causes less fabric yellowing and measuring cup residue than an all fatty acid formula when used with the above liquid bleach.

Example II

Other compositions of the present invention, which can be prepared as in Example I, are as follows:

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		Wt.8				4
5	Components	<u>A</u>	B	<u>c</u>	D	
5	<pre>1,12-Diperoxydodecanedioic acid*</pre>	12.5	-	25.0		
40	1,9-Diperoxyazelaic acid*	-	15.0	-	_	
10	Water	73.0		56.0	65.0	
15	C ₁₃ linear alkylbenzene sulfonic acid		3.0		-	:
15	C _{11.4} linear alkylbenzene sulfonic acid	•	-	• ,	3.0	
20	Sodium cumene sulfonate	_	2.0			
	Magnesium sulfate	6.6		10.5	9.2	
	Sodium sulfate	3.1		2.5	-	
25	Potassium sulfate	_	- .	_	1.0	
	Suds suppressor	_	0.1	0.02	•	
	Dipicolinic acid	0.01		0.01		
<i>30</i>	Sodium hydroxide to pH:	3.8		3.35		٠.
	Viscosity (cps at 20°C)	450			**	
<i>35</i>	*Average particle size preparation.	about	2-5		ns, a	Eter
	** Within the range of 50-1	000-	•	· · · · · · · · · · · · · · · · · · ·		

Example III

After storage of an about 22.3 kg sample of the liquid bleach mixture of Example I for about 8 months at about 20°C, a clear aqueous layer (about 6 kg) was removed from the bottom of the sample and the remainder was analyzed to contain the following:

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٠	Components	Wt.8
	1,12-Diperoxydodecanedioic	
<i>50</i>	acid (DPDA)	16.3
	Water	57.0
	Suds suppressor	0.11
<i>55</i>	C ₁₃ linear alkylbenze	0.11
	sulfonic acid	3.4
	Sodium cumene sulfonate	1.8
<i>60</i>	Dipicolinic acid	0.01

Components	Wt.8
Sodium sulfate	3.5
Magnesium sulfate	9.2
Miscellaneous	balance

The composition had a viscosity of about 850 cps, measured at 20°C. An additional 6.4 parts of sodium cumene sulfonate (50% active) was added to 100 parts of the composition to reduce its viscosity to about 240 cps at 20°C. This composition had a pH of about 2.6. Its pH was adjusted to about 3.15 by adding a 50% solution of sodium hydroxide, resulting in a finished liquid bleach composition containing about 15.5% DPDA.

The above liquid bleach composition is preferably used in combination with the following liquid detergent composition, which was prepared by adding the components to a mixing tank in the order listed with continuous mixing.

	8	Wt. 8	Wt. 8	20
Components	Assay	Product	Stock	20
C ₁₃ linear alkylbenzene		44		
sulfonic acid	45.0	7.87	17.49 ¹	<i>25</i>
Sodium C ₁₄₋₁₅ alkyl poly-		·		· .
ethoxylate (2.25) sulfate	48.4	11.86	24.512	-
Propylene glycol	100.0	8.38	3.53	<i>30</i>
Sodium diethylenetriamine		,		
pentaacetate	41.0	0.30	0.73	÷ .
Brightener mix	100.0	-	6.70 ³	<i>35</i>
Monoethanolamine	100.0	4.5	2.50	
C ₁₂₋₁₃ alcohol polyethoxy-	•			
late (6.5)*	100.0	4.93	2.93	40
Ethanol	92.0	3.94	-	
Sodium hydroxide	50.0	4.19	5.38	
Potassium hydroxide	45.0	1.18	2.62	45
C ₁₂₋₁₄ fatty acid	100.0	9.86	9.86	
Citric acid	50.0	3.94	7.88	•
Calcium formate	10.0	0.12	1.20	50
Sodium formate	30.0	0.86	2.77	
C ₁₂ alkyltrimethylammonium				
chloride	37.0	0.6	1.62	<i>55</i>

	Components	Assay	Wt. % Product	Wt. %
5	TEPA-E 15-18 ** pH trim to 10.5	80.0	1.97	2.46
10	Protease enzyme (2.0 AU/g) Amylase enzyme (375 AM. U/g)	100.0	0.74	0.74
	Dye	100.0	0.16 0.08	0.16 0.08
15	Perfume Water 1_	100.0	0.25 to 100%	0.25 6.59
20	Paste also contains 1.4 monoethanolamine, 25% propylo 2 Paste also contains 16.	ene alvad	ol and on	169
	nydroxide, and 30.3% water.			
25	3Contains 7.46% monoethanola polyethoxylate (6.5)*, 5 brightener.	mine, 29	.82% C ₁₂ -: water, a	alcohol nd 3.07%
<i>30</i>	* Alcohol and monoethoxyla	ated alco	hol remove	a

hol and monoethoxylated alcohol removed.

Tetraethylene pentaimine ethoylated with 15-18 moles (avg.) of ethylene oxide at each hydrogen site.

The compositions are preferably used in a volume ratio of detergent composition to liquid bleach of about 4:1. The detergent composition is designed for a usage level of about 0.5 cups in a tyical U.S. laundering process. This delivers a concentration of product in the wash water of about 0.2% by weight. Usage of about 0.125 cups (i.e., about 30 ml) of the liquid bleach would deliver about 10 ppm of available oxygen to the wash water. The detergent composition and liquid bleach are preferably simultaneously codispensed from a single dosing, dual compartment cup at a volume ratio of detergent to bleach of about 4:1.

Claims

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1. A stable liquid bleach composition comprising, by weight:

- (a) from about 10% to about 25% of water-insoluble diperoxyacid particles of the formula HOOOC(CH₂)_nCOOOH, wherein n is from about 7 to about 14, said particles having an average size of from about 0.5 to about 15 microns;
 - (b) from about 2% to about 6%, on an acid basis, of a C_{11} - C_{13} linear alkylbenzene sulfonate surfactant;
 - (c) from about 0% to about 8%, on an acid basis, of cumene sulfonate;
 - (d) from about 5% to about 15% of magnesium sulfate;
 - (e) from 0% to about 7% sodium or potassium sulfate; and
 - (f) from about 40% to about 78% water
 - said composition containing from about 3% to about 14% of (b) and (c), from about 5% to about 16% of (d) and (e), and from about 12% to about 30% of (b), (c), (d) and (e); the weight ratio of (a) to (d) being less than about 3:1; and said composition having a pH of from about 2 to about 4.5 and a viscosity of from about 50 to about 1000 cps at 20°C.
 - 2. The composition of Claim 1 wherein the diperoxyacid is 1,12-diperoxydodecanedioic acid.
 - 3. The composition of Claim 1 wherein the diperoxyacid particles have an average size of from about 0.5 to about 10 microns.
 - 4. The composition of Claim 1 wherein (b) is a C_{13} linear alkylbenzene sulfonate.
 - 5. The composition of Claim 1 wherein the composition has a viscosity of from about 75 to about 500

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cps at 20°C.

- 6. The composition of Claim 5 wherein (b) is a C_{13} linear alkylbenzene sulfonate.
- 7. The composition of Claim 6 comprising from about 2% to about 4% of C₁₃ linear alkylbenzene sulfonate and from about 1% to about 6% of cumene sulfonate.
- 8. The composition of Claim 7 comprising from about 8% to about 12% of magnesium sulfate from about 2% to about 6% of sodium sulfate.
- 9. The composition of Claim 8 comprising from about 14% to about 20% of the 1,12-diperoxydode-canedioic acid.
- 10. The composition of Claim 9 having a viscosity of from about 100 to about 350 cps at 20°C.

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EUROPEAN SEARCH REPORT

87 87 0040 EP

Category	Citation of docum	nent with indication, where appropriate, of relevant passages	Relevan to claim	
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r	US-A-3 996 152 al.) * claims 1-3 *	(J.B. EDWARDS et	1,5	
	,, ,,	(J.P. HUTCHINS lines 47-54; claims	1,2,4	
,P E	P-A-0 201 958 claims 1-3 *	(AKZO N.V.)	1,2	TECHNICAL FIELDS SEARCHED (Int. CI.4)
*	P-A-O 075 419 AMBLE CO.) page 25, tabl le 2A, claims	e lA nage 27 +-	1,2	C 11 D 3/00
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- X: particularly relevant if taken alone
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 A: technological background
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- E: earlier patent document, but published on, or after the filing date
 D: document cited in the application
 L: document cited for other reasons
- à : member of the same patent family, corresponding document